PAT-NO: JP411060634A

DOCUMENT-IDENTIFIER: JP 11060634 A

TITLE: ETHYLENE POLYMER HAVING RESTRAINED AMORPHOUS PORTION

PUBN-DATE: March 2, 1999

INVENTOR-INFORMATION:

NAME   COUNTRY

YAHIRO, SHUJI

INT-CL (IPC): C08F010/02 , C08F004/645 , C08F210/16

ABSTRACT:

PROBLEM TO BE SOLVED: To obtain ethylene polymers excellent in moldability, sufficiently restrained in the amorphous portion and particularly excellent in ductile fracture resistance.

SOLUTION: Ethylene polymers having a restrained amorphous portion are ethylene homopolymers or copolymers of ethylene and a 3-20C α-olefin having (A) a melt index, under a load of 2.16 kg at 190°C, of 0.001-1,000 g/min, (B) a density of 0.90 g/cm3-0.985 g/cm3, (C) a molecular weight distribution, measured by gel permeation chromatography, of 3-7 and (D) a ratio (T_2a/T_2c) of the spin-spin relaxation time T_2a (microsecond) of the amorphous portion, measured by the 1H pulsed NMR at 40°C to the spin-spin relaxation time T_2c (microsecond) of the crystalline portion, being not greater than 7.2.

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the ethylene polymer which is excellent in a moldability and has the restrained amorphous section.
[0002]
[Description of the Prior Art] A polyolefine, especially polyethylene are lightweight, since it excels in economical efficiency, therefore, are easily fabricated by melting fabrication of extrusion molding, blow molding, injection molding, etc., and are widely used for it. However, although the polyethylene which carried out the polymerization by the Ziegler catalyst widely used from the former is satisfying in a moldability, machine physical properties, especially its environmental-stress-cracking-proof nature ("ESCR" is called below.) are inadequate. Especially in large-sized mold goods, a raise in the rigidity of polyethylene is required and the ethylene polymer which was excellent in ESCR also in such polyethylene of high rigidity is demanded.
[0003] On the other hand, although the so-called Phillips catalyst which made the inorganic-oxide solid-state support a chrome oxide is excellent in a moldability, machine physical properties are poor. Using the ethylene polymer of these former, when the solid-state structure of various machine physical properties and an ethylene polymer was examined wholeheartedly, the following things became clear. The amorphous section in the conventional ethylene polymer was not fully restrained, but the ethylene polymer which has such the amorphous section caused deformation easily to external force, such as tension, and, as a result, that it is very easy to be destroyed made the ethylene polymer clear.
[0004] then, the attempt which manufactures the ethylene polymer by which machine physical properties were improved by using the catalyst adjusted from a metallocene compound, aluminoxane, etc. in recent years -- JP,58-19309,A -- said -- 60-35006 -- said -- 60-35007 -- said -- 61-130314 -- said -- 61-221208 -- said -- it is indicated by official reports, such as 62-121709 and 62-121711 these attempts -- an ethylene polymerization -- insertion of a comonomer in the living body -- controlling -- an ethylene polymerization -- it is going to control the crystal section in the living body -- it tries and comes out As for these ethylene polymer, insertion in the molecule of a comonomer is controlled extremely. Furthermore, in the solid-state structure of these ethylene polymer, the amorphous section is restrained and is excellent in machine physical properties. However, these ethylene polymer of molecular weight distribution is narrow, and, for the reason, cannot satisfy a moldability.
[0005] Moreover, the attempt which manufactures the ethylene polymer which is satisfied [with keeping molecular weight distribution narrow according to a restricted geometry addition catalyst (JP,3-163088,A), and inserting long-chain branching into the molecule] of both fabricating-operation nature and machine physical properties is made. However, the ethylene polymer obtained when this catalyst is used for a solution polymerization method has the problem of being inferior to ESCR, in comparison with the ethylene polymer by the Ziegler catalyst which has the same melt index.
[0006]
[Problem(s) to be Solved by the Invention] this invention is made in view of the above-mentioned

trouble, and is to offer the specific ethylene polymer excellent in a moldability and machine physical properties.

[0007]

[Means for Solving the Problem] As a result of inquiring wholeheartedly, this invention person was excellent in the moldability, found out the ethylene polymer by which the amorphous section was restrained, and reached this invention. this invention relates to the ethylene polymer characterized by satisfying each conditions of (D) from following (A). Namely, they are an ethylene homopolymer or the copolymer of ethylene and the alpha-olefin of carbon numbers 3-20. (A) Melt index in 2.16kg load in 190 degrees C ("MI" is called below.) 0.001-1000g / 10 minutes, (B) density 0.90g/cm3 -0.985g/cm3, (C) gel PAMESHON chromatography ("GPC" is called below.) Measured molecular weight distribution ("Mw/Mn" is called below.) they are 3-7, and (D)40 degree C -- it can set the ratio of spin-spin-relaxation-time T2c (microsecond) of the crystal section and spin-spin-relaxation-time T2a (microsecond) of the amorphous section for which it asked by the 1H pulse NMR -- it is related with the ethylene polymer to which T2 a/T2c comes out and is characterized by a certain thing 7.2 or less

[0008] this invention is explained in detail below. the ethylene polymer of this invention -- an ethylene homopolymer or ethylene, and carbon numbers 3-20 -- it is a random copolymer with the alpha olefin of 4-20 preferably As an alpha olefin of carbon numbers 3-20, a propylene, butene-1, a pentene 1, the 3-methylbutene 1, a hexene 1, 4-methyl pentene 1, an octene 1, DESEN 1, tetrapod DESEN 1, hexa DESEN 1, octadecene 1, ray KOSEN 1, etc. can be used. Furthermore, vinyl compounds, such as a vinyl cyclohexane or styrene, and its derivative, can also be used. Moreover, ****** is also good at the random 3 yuan polymer which carries out little content of the disconjugate polyene, such as 1, 5-hexadiene, 1, and 7-OKUTA diene, if needed.

[0009] MI of the ethylene polymer of this invention -- 0.001-1000g/-- it is a range for 0.005-600g / 10 minutes preferably for 10 minutes MI cannot manufacture 0.001g / ethylene polymer for less than 10 minutes with the specific catalyst used by this invention. On the other hand, when MI exceeds 1000g / 10 minutes, the intensity of mold goods falls. In addition, MI is ASTM. According to D1238, it measured by 2.16kg load in 190 degrees C.

[0010] the density of the ethylene polymer of this invention -- 0.90 g/cm3 - 0.985 g/cm3 -- desirable -- 0.915 g/cm3 - 0.980 g/cm3 It is a range. Density here measures mold goods with a density-gradient pipe as it is. Density is 0.985 g/cm3. The ethylene polymer to exceed cannot be manufactured with the specific catalyst used in this invention. The ethylene polymer of this invention needs to manufacture by the slurry regime, specific manufacture conditions, i.e., ethylene polymer, in a slurry regime, as for an ethylene polymer, manufacture becomes impossible, and the problem that Mw/Mn of an ethylene polymer becomes narrow as a result generates it under at the minimum of this density.

[0011] moreover, Mw/Mn which measured Mw/Mn of the ethylene polymer of this invention by GPC -- 3-7 -- it is the range of 3.5-7 preferably When Mw/Mn is less than three, an ethylene polymer has an inadequate moldability, and when Mw/Mn exceeds from 7, there is a problem that the machine physical properties of an ethylene polymer fall. In addition, it is desirable to set up the molecular weight distribution of an ethylene polymer so that it may have a range [as / whose values which broke the melt index in 21.6kg load in 190 degrees C by the melt index in 2.16kg load in 190 degrees C are 19-40]. the measuring device used for measurement of GPC -- 150made from Waters-C as ALC/GPC and a column -- the product made from Shodex -- AT-807S and TSK-gelGMH-H6 by TOSOH CORP. were made in-series, and were used, the trichlorobenzene was used for the solvent, and it measured at 140 degrees C In addition, in order to satisfy above-mentioned range Mw/Mn in this invention, a certain specific catalyst was used and the process which carries out the polymerization of the ethylene polymer by the slurry regime was used.

[0012] The ethylene polymer of this invention needs to have a certain specific solid-state structure. that is, it can set at 40 degrees C the ratio of spin-spin-relaxation-time T2c (microsecond) of the crystal section and spin-spin-relaxation-time T2a (microsecond) of the amorphous section for which it asked by the 1H pulse NMR -- T2 a/T2c needs to be 7.2 or less A spin spin relaxation time here is a scale showing the maneuverability of each part, and if the thickness of the crystal section becomes thick, the

relaxation time of the crystal section will become short. On the other hand, although the relaxation time of the amorphous section will become short if the amorphous section is enough restrained by the crystal section, when the distribution of the thickness of the crystal section is large, a part of amorphous sections are not fully restrained by the crystal section, but, as a result, the relaxation time of the amorphous section of an ethylene polymer becomes long, for example. If the ratio of this relaxation time exceeds 7.2, restraining [of the amorphous section] will become inadequate and the machine physical properties of an ethylene polymer will become poor. It is six or less still more preferably 6.5 or less preferably.

[0013] This relaxation time divides into two components the decay curve (FID) of the spin spin relaxation time obtained by J.Chem.Phys., such as west, and the method announced by 82 and 9 (1985), for example, the solid ******ing method, by the least-squares method by computer. The component which decreases once the component decreased quickly for a short time in a long time belongs to the amorphous section, carries out fitting of the decay curve to the crystal section using the following formula, and asks it for the relaxation time of each part.

L1 exp(-t/T2c)+L2 exp2 (here, t is time and L1+L2 =1.) (-t/T2c)

Furthermore, as for this T2c, it is desirable that they are ten or less microseconds. When this value exceeds 10 microseconds, the rigidity of an ethylene polymer falls.

[0014] furthermore, the thickness of the crystal section -- an ethylene polymerization -- it already reports that there are a tie molecule in the living body and correlation -- having -- **** -- the amount of this tie molecule -- an ethylene polymerization -- the endurance over ductile fractures, such as ESCR, improves especially, so that many [inside of the body] That is, the melt index in 2.16kg load in 190 degrees C is density Yg/cm3 at Xg / 10 minutes. Ethylene homopolymer, And the AKO stakes band of the direction of the first major axis for which the melt index in 2.16kg load in 190 degrees C asked by the laser Raman spectroscopy in the ethylene copolymer of density Ycg/cm3 for Xcg / 10 minutes ("LAM" is called below.) The case where the frequency nu of a peak (cm-1) is expressed with the following formula is desirable.

0.0768xLogX+30 (Y-Yc)+10.3(cm-1) <nu (cm-1)

In the case of [, however an ethylene homopolymer, it is 0.0768xLogX+10.3(cm-1) <nu(cm-1)].

[0015] this LAM band -- an ethylene polymerization -- there is correlation with the thickness of the crystal section in the living body -- for example, Journal of Polymer Science:Polymer Physics It is indicated by Edition, 19 volumes, and 1593-1609 pages (19783 years). The lamellae thickness of an ethylene polymer is so thin that the frequency of this LAM is high as a general trend. Although surely the density of an ethylene polymer falls the density of an ethylene polymer a fall **** case by adding a comonomer in the conventional ethylene polymer, still, the thickness of the crystal section is thick, consequently there are few amounts of the tie molecule in an ethylene polymer. laser-Raman-spectroscopy analysis of this application -- setting -- Ramaonor T-6400 type -- using -- a light source laser-power 300mW argon laser, 90 measurement arrangement dispersion, 640mm triple monochromator of spectroscopes, 50 micrometers of slits, and detector Yvon 1024x256 was used.

[0016] Next, the process of the ethylene polymer of this invention is described. Using the titanium compound of which eta combination was done at least with the (a) support matter, a (b) organoaluminium compound, the borate compound that has (c) active hydrogen, (d) cyclopentadienyl, or the substituent cyclopentadienyl group, and the support catalyst by which shell adjustment was carried out, by the slurry regime, the ethylene polymer of this invention carries out copolymerization of an ethylene independent or ethylene, and the alpha olefin of carbon numbers 3-20, and is obtained.

[0017] As a support matter (a), ****** is also good at any of organic support and inorganic support. As organic support, preferably The alpha olefin polymer of the (1) carbon numbers 2-10, For example, polyethylene, polypropylene, a polybutene 1, an ethylene propylene rubber, An ethylene butene-1 copolymer, ethylene hexene 1 copolymer, A propylene butene-1 copolymer, a propylene divinylbenzene copolymer, (2) An aromatic unsaturated-hydrocarbon polymer, for example, polystyrene, a styrene divinylbenzene copolymer, And (3) polar-group content polymer, for example, polyacrylic ester, a polymethacrylic acid ester, the poly acrylic nitril, a polyvinyl chloride, a polyamide, a polycarbonate,

etc. are mentioned.

[0018] As inorganic support, the (4) inorganic oxide 2, for example, SiO, and aluminum 2O3, MgO, TiO2, B-2 O3, CaO, ZnO, BaO, ThO, SiO2-MgO, SiO2-aluminum 2O3, SiO2-MgO, SiO2-V2 O5 etc. -- (5) inorganic halogenated compound for example, MgCl2, AlCl3, and MnCl2 etc. -- a (6) inorganic carbonate -- A sulfate, a nitrate 3, for example, Na2 CO, K2 CO3, and CaCO3, MgCO3, aluminum2 3 (SO4), BaSO4, KNO3, and Mg (NO3)2 etc. -- (-- seven --) -- inorganic -- a hydroxide -- for example, -- Mg -- (-- OH --) -- two -- aluminum -- (-- OH --) -- three -- calcium -- (-- OH --) -- two etc. -- it is illustrated The most desirable support matter is a silica. Although the particle diameter of support is arbitrary, generally it is 10-1000 micrometers still more preferably 5-2000 micrometers preferably 1-3000 micrometers.

[0019] The above-mentioned support matter is processed by the organoaluminium-compound (b). As an example of a desirable organoaluminium compound A trimethylaluminum, a triethylaluminum, triisobutylaluminum, Trihexyl aluminium, trioctyl aluminum, tridecyl aluminium, Diethyl aluminum monochrome chloride, diisobutyl aluminum monochrome chloride, Ethylaluminiumsesquichloride, ethyl aluminum dichloride, Alkylaluminum hydrides, such as a diethyl aluminum hydride and a diisobutyl aluminum hydride, Diethyl aluminum ethoxide, dimethyl aluminum NYUU trimethyl siloxide, Alumoxane, such as aluminum alkoxides, such as a dimethyl aluminum phenoxide, methylalumoxane, ethyl aluminum Korean geisha, isobutyl aluminum Korean geisha, and methyl isobuthylalumoxane, etc. is mentioned. A trialkylaluminium, an aluminum alkoxide, etc. are [among these] desirable. They are a trimethylaluminum, a triethylaluminum, and triisobutylaluminum most preferably.

[0020] In the support catalyst furthermore used in the process of the ethylene polymer of this invention, the borate compound which has active hydrogen which can express with the following general formula is used. the time of this borate compound being an activator which reacts with titanium compound (**) carried out, and changes (**) into a cation eta combination with cyclopentadienyl or a substituent cyclopentadienyl group, and the group (T-H) which has active hydrogen in the borate compound of a parenthesis supporting these borate compound to the support matter -- support and a chemical bond -- or physical combination is carried out

[0021] [B-Qn(Gq(T-H) r) z] A+ -- here, B expresses boron G expresses a multi-unity hydrocarbon radical, as a desirable multi-unity hydrocarbon, it is the alkylene of carbon numbers 1-20, a propine, and an ARUARIREN radical, and a phenylene, a screw phenylene, naphthalene, a methylene, ethylene, 1, 3-propylene, 1, 4-butadiene, p-phenylene methylene, etc. are mentioned as a desirable example of G. Combination of r+1, i.e., one combination, combines with a borate anion, and the combination r of others of G combines the multi-unity radical G with a machine (T-H).

[0022] T in the above-mentioned general formula expresses -O-, -S-, -NR-, or -PR-, and R expresses a hydronalium phenyl-isocyanate radical, a TORIHIDOROI phenyl-isocyanate silyl radical, a TORIHAIDORO phenyl-isocyanate germanium radical, or a hydride here. q is 1 preferably or more in one. as an T-H group -OH, -SH, -NRH or -PRH, and here -- R -- carbon numbers 1-18 -- it is the hydro phenyl-isocyanate radical or hydrogen of carbon numbers 1-10 preferably Desirable R group is alkyl aryl of an alkyl, cycloalkyl, an allyl compound, an arylated alkyl, or carbon numbers 1-18. - For example, -C(O)-OH, -C(S)-SH, -C(O)-NRH, and C(O)-PRH are sufficient as OH, -SH, -NRH, or -PRH. The basis which has the most desirable active hydrogen is a -OH basis. Q -- a hydride and a dihydrocull building amide -- they are a dialkyl amide, halide, a high drocarbil oxide, an alkoxide, an allyl-compound oxide, the high drocarbil, a substitution highness drocarbil radical, etc. preferably n+z is 4 here.
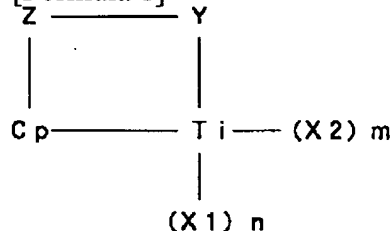
[0023] As [B-Qn(Gq(T-H) r) z] of the above-mentioned general formula For example, triphenyl (hydroxyphenyl) borate, JIFENI rouge (hydroxyphenyl) borate, Triphenyl (2, 4-dihydroxy phenyl) volley TOTORI (p-tolyl) (hydroxyphenyl) borate, TORISU (pentafluorophenyl) (hydroxyphenyl) borate, TORISU (2, 4-dimethylphenyl) (hydroxyphenyl) borate, TORISU (3, 5-dimethylphenyl) (hydroxyphenyl) borate, TORISU (3, 5-G trifluoromethyl phenyl) (hydroxyphenyl) borate, TORISU (pentafluorophenyl) (2-hydroxyethyl) borate, TORISU (pentafluorophenyl) (4-hydroxy butyl) borate, TORISU (pentafluorophenyl) (4-hydroxy cyclohexyl) borate, TORISU (pentafluorophenyl) (4-(4, -

hydroxyphenyl) phenyl) borate, TORISU (pentafluorophenyl) (6-hydroxy 2-naphthyl) borate etc. is mentioned, and it is tris (pentafluorophenyl) (4-hydroxy phenyl) borate most preferably. Furthermore, it is -OH basis of the above-mentioned borate compound. - What was replaced by NHR (R is a methyl, ethyl, and t-butyl here) is desirable.

[0024] as the opposite cation of a borate compound -- a carbonium cation and fatty tuna -- a pill RYUUMU cation, an ammonium cation, an oxonium cation, a sulfo NYUMU cation, and a phosphonium cation are mentioned Moreover, the metaled cation and the cation of an organic metal to which it confidence is easy to be returned are also mentioned. As an example of these cations, triphenyl carbonium ion, Diphenyl carbonium ion, cyclo HEPUTATORINIUMU, indie NIUMU, Triethyl ammonium, TORIPURO pill ammonium, tributyl ammonium, Dimethylannmonium, dipropyl ammonium, dicyclohexyl ammonium, Trioctyl ammonium, N, and N-dimethylannmonium, diethyl ammonium, 2, 4, 6-pen reservoir chill ammonium, N, and N-dimethylbenzyl ammonium, G (i-propyl) ammonium, dicyclohexyl ammonium, Triphenyl phosphonium, TORIHOSUHONIUMU, a TORIJI methylphenyl phosphonium, A TORI (methylphenyl) phosphonium, triphenyl phosphonium ion, A triphenyl oxonium ion, a triethyl oxonium ion, pilus NIUMU, a complex ion, golden ion, platinum ion, a copper ion, PARAJUUMUION, mercury ion, ferro SENIUMU ion, etc. are mentioned. An ammonium ion is desirable also in especially inside.

[0025] In this invention, the titanium compound (d) of which eta combination was done with the cyclopentadienyl or the substituent cyclopentadienyl group which can be expressed with the following general formula is used.

[Formula 1]

$$\begin{array}{ccc} Z & \rule{2cm}{0.4pt} & Y \\ | & & | \\ | & & | \\ Cp \rule{2cm}{0.4pt} & Ti \rule{0.5cm}{0.4pt} & (X2)\,m \\ & | & \\ & (X1)\,n & \end{array}$$

[0026] The titanium atom whose Ti is the oxidation state of +2, +3, and +4, and Cp are the cyclopentadienyl or the substituent cyclopentadienyl groups to carry out eta combination here at titanium, X1 is an anionic ligand, and X2 is a neutral conjugated-diene compound. n+m is 1 or 2 and Y is -O-, -S-, -NR-, or -PR-. Z SiR2, CR2, SiR2-SiR2, and CR2 CR2, CR=CR, CR2SiR2, GeR2, and BR2 it is -- in each case, R is chosen from those combination with hydrogen, hydrocarbyl, silyl, gel MYUMU, cyano, halos or these combination things, and the non-hydrogen atom to 20 pieces

[0027] It is the cyclopentadienyl group which one sort or the hydrocarbyl of the carbon numbers 1-20 beyond it, the halo hydrocarbyl of carbon numbers 1-20, a halogen or the hydrocarbyl substitution of carbon numbers 1-20, the cyclopentadienyl replaced with the 14th group metalloid machine, indenyl, tetrahydro indenyl, fluorenyl, or OKUTA fluorenyl was mentioned as a substituent cyclopentadienyl group, and was preferably replaced by the alkyl group of carbon numbers 1-6.

[0028] As X1 and X2, it sets, for example to the above-mentioned general formula. n is 2 and m is 0. If the oxidation number of titanium is +4, X1 will be chosen from a methyl and a benzyl. n is 0 further. if n is [1 and m of the oxidation number of titanium] +3 in 0 -- X1 -- a 2-(N and N-dimethyl) amino benzyl -- if the oxidation number of titanium is +4 further -- X1 -- 2-butene-1 and 4-diyl -- In 1, if m is +2, it is [the oxidation number of titanium of X2] 1, 4-diphenyl 1,3-butadiene or 1, and 3-pentadiene.

[0029] Although the catalyst of this invention is acquired by making a component (a) support a component (b), a component (c), and a component (d) Although the method of making a component (d) support from a component (b) is arbitrary, generally A component (b), A component (c) and a component (d) are dissolved into the inert solvent which can dissolve each. Without being the range in which a solid-state does not deposit after dissolving the method of distilling off a solvent and a component (b), a component (c), and a component (d) in an inert solvent, after mixing with a component

(a) How to add the component (a) of an amount which condenses this and can hold the whole quantity of the following concentration liquid in a particle, How to make a component (a) support a component (b) and a component (c) first, and to make a component (d) support subsequently, The method of making a component (a) support the method and the component (a) which make serial support a component (b), a component (d), and a component (c), a component (b), a component (c), and a component (d) by co-grinding etc. is illustrated.

[0030] Generally the component (c) and the component (d) of this invention are a solid-state, and since a component (b) has pyrophoricity, these components may be diluted and used for an inert solvent in the case of support. As an inert solvent used for this purpose, halogenated hydrocarbons or such mixture, such as aromatic-hydrocarbons [, such as alicycle group hydrocarbon; benzene, such as aliphatic hydrocarbon; cyclopentanes, such as a propane, butane, a pentane, a hexane, a heptane, an octane Deccan, a dodecane, and lamp oil, a cyclohexane, and a methylcyclopentane, toluene, and a xylene,]; and ethyl chloride, chlorobenzene, and dichloromethane, etc. can be mentioned, for example. As for this inert hydrocarbon solvent, it is desirable to remove and use impurities, such as water, oxygen, and a sulfur content, using a drying agent, an adsorbent, etc.

[0031] As opposed to 1g of component (a)s a (b) by aluminum atom conversion 1x10-5 to 1xten - one mol, The range of 1xten - seven mols - 1xten - three mols of 1xten - seven mols - 1xten - three mols of 5xten - seven mols - 5xten - four mols and (d)s of 1xten - four mols - 5xten - two mols and a (c) is 5xten - seven mols - 5xten - four mols preferably. The amount of each [used] and the support method are determined by the scale in ******, economical efficiency, a powder property, and a reactor etc. for the purpose of removing the organoaluminium compound which is not supported by support, a borate compound, and a titanium compound, an inert hydrocarbon solvent can be used for the acquired support catalyst, and it can be come out of it, and it can also be washed by methods, such as a decantation or filtration

[0032] Performing operation of a series of above-mentioned dissolutions, contact, washing, etc. at the temperature of -30-degree-C or more 150-degree-C or less range chosen for every unit operation of the is recommended. The more desirable range of such temperature is 0 degrees C or more 100 degrees C or less. It is desirable to perform a series of operations of acquiring a solid-state catalyst by this invention, under the dry inert atmosphere. also saving the solid-state catalyst of this invention by the slurry regime distributed in the inert hydrocarbon solvent -- or it can dry and can also save by the solid state

[0033] When performing the polymerization of an ethylene polymer, generally, three to 30 atmospheric pressure is preferably suitable for the polymerization preassure force one to 100 atmospheric pressure, and 20-115-degree C 50-105 degrees C are preferably suitable for polymerization temperature. However, the temperature to which the ethylene system polymer to generate can maintain a slurry regime substantially is an upper limit, and the upper limit of temperature has the problem that molecule end double combination of an ethylene polymer increases, when exceeding this value. Such upper limit temperature may change depending on the density and the solvent to be used of the ethylene system copolymer to generate.

[0034] As a solvent used for slurry method, the inert hydrocarbon solvent previously indicated by this invention is suitable, and an isobutane, an isopentane, a heptane, a hexane, an octane, etc. are suitable especially. The comonomer which can be used by this invention is an alpha olefin expressed with the following general formula.

H2-C=CHR (R is the alkyl group of carbon numbers 1-18, or the aryl group of carbon numbers 6-20 among a formula, and an alkyl-group is the shape of a straight chain, a letter of branching, or annular.)

[0035] As such a comonomer, for example A propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecen, 1-tetrapod decene, 1-hexa decene, It is chosen out of the group which consists of 1-octadecene, 1-ray KOSEN, a vinyl cyclohexane, and styrene. The annular olefin of carbon numbers 3-20, for example, a cyclopentene, a cyclo heptene, Norbornene, 5-methyl-2-norbornene, tetracyclo dodecen, And the 2-methyl -1.4, 5.8-dimethano - It is chosen out of the group which consists of 1, 2, 3, 4,a [4], 5, 8, and 8a-octahydronaphthalene. It is chosen out of the group which consists of the shape of a straight chain of carbon numbers 4-20, the letter of branching or an

annular diene, for example, 1,3-butadiene, 1, 4-pentadiene, 1, 5-hexadiene, 1, a 4-hexadiene, and a cyclohexadiene. Especially in this invention, a propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecen, 1-tetrapod decene, 1-hexa decene, 1-octadecene, 1-ray KOSEN, etc. are suitable.

[0036] Moreover, although the polymerization of ethylene or ethylene, and an alpha olefin is possible for the catalyst by this invention only at it, it is also possible to use it, making an organoaluminium compound live together as an addition component because of prevention of poisoning of a solvent or the system of reaction. As an example of a desirable organoaluminium compound A trimethylaluminum, a triethylaluminum, triisobutylaluminum, Alkylaluminum, such as trihexyl aluminium, trioctyl aluminum, and tridecyl aluminium; Diethyl aluminum monochrome chloride, Diisobutyl aluminum monochrome chloride, ethylaluminiumsesquichloride, Ethyl aluminum dichloride, a diethyl aluminum hydride, Alkylaluminum hydrides, such as a diisobutyl aluminum hydride; Diethyl aluminum ethoxide, Aluminum alkoxides, such as dimethyl aluminum NYUU trimethyl siloxide and a dimethyl aluminum phenoxide; alumoxane, such as methylalumoxane, ethyl aluminum Korean geisha, isobutyl aluminum Korean geisha, and methyl isobuthylalumoxane, etc. is mentioned. A trialkylaluminium, an aluminum alkoxide, etc. are [among these] desirable. They are a trimethylaluminum, a triethylaluminum, and triisobutylaluminum most preferably.

[0037] the ethylene polymer of this invention -- it independence -- or even if it mixes, you may use It is good to use as a bimodal constituent which mixed the high ethylene polymer of MI and the polymer of a low MI especially. You may denaturalize using the blend with inorganic material, such as other polymer and a filler, and talc, an alloy, and denaturation technology still better known generally. Moreover, you may add additives, such as an antioxidant, illuminant-proof, and a release agent. The ethylene polymer of this invention is fabricated by the well-known fabricating methods, such as injection molding, blow molding, a pipe, a film, and compression molding.

[0038]

[Example] Although an example explains this invention below, these do not limit the range of this invention. Each physical properties in this invention were measured by the following method.

** MI is ASTM. It is the value measured by 190 degrees C and 2.16kg of loads according to D1238.

** The scale (MIR) MIR of fabricating-operation nature is the value broken by MI which measured the value of MI measured by 21.6kg of loads in the temperature of 190 degrees C by 2.16kg of loads in the temperature of 190 degrees C. It excels in fabricating-operation nature, so that this value is large.

** Mw/Mn: -- the measuring device used for measurement -- 150made from Waters-C as ALC/GPC and a column -- the product made from Shodex -- AT-807S and TSK-gelGMH-H6 by TOSOH CORP. were made in-series, and were used, and it measured at 140 degrees C using the trichlorobenzene which contains 10 ppm IRUGA NOx 1010 in a solvent In addition, the calibration curve was created using mono dispersion commercial polystyrene as the standard substance.

[0039] ** Raman analysis : 1010; 500 ppm of IRUGA NOx were added to the ethylene polymer, and it corned with the monopodium push appearance machine at 190 degrees C. the obtained pellet -- a press-forming machine -- 200 degrees C and 100 kg/cm2 melting is carried out for 3 minutes -- making -- after that 10degree-C/a part -- it cooled and the plate with a thickness of 2mm was created This plate is used and it is Ramaonor as a measuring device. T-6400 type, a light source laser-power 300mW argon laser, 90 measurement arrangement dispersion, 640mm triple monochromator of spectroscopes, 50 micrometers of slits, detection machine Yvon It measured at 25 degrees C using 1024x256, and the peak value of the frequency of a LAM band was calculated. .

** Machine physical properties (a) Rigidity: Since rigidity is determined by density, it evaluated rigidity by density. Density measured the plate used by the above-mentioned Raman analysis using the density-gradient pipe.

(b) ESCR : F50 by the BTM method measured according to above-mentioned pellet JIS-K -6760 was made into the value of ESCR.

[0040] ** a pulse NMR:ethylene polymer pellet -- a press-forming machine -- 200 degrees C and 100 kg/cm2 melting is carried out for 3 minutes -- making -- after that 10degree-C/a part -- it cooled and the

2mm plate was obtained The obtained plate was started, and it put into the sample pipe, and measured at 40 degrees C. measurement of Pulse NMR -- made in Bruker -- using PC-20, the pulse used the solid ******ing method After changing the decay curve of the obtained spin spin relaxation with the connected auto NIKUSU tolan jar and taking it out to a computer, by the least-squares method, it was divided into the component decreased quickly for a short time, and a long time or the component decreased once, carried out fitting of the decay curve using the following formula, and found the relaxation time of each part.

L1 exp(-t/T2c)+L2 exp2 (here, t is time and L1+L2 =1.) (-t/T2c)

[0041] (Example 1) 6.2g (8.8mmol) triethyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate was added to 4l. toluene, and was stirred for 30 minutes 90 degrees C. Next, 40ml of toluene solutions of the trihexyl aluminium of 1 mol/l was added to this solution, and it stirred for 1 minute at 90 degrees C. On the other hand, the silica P-10 (made in [Fuji SHIRISHIA] Japan) was processed by the nitrogen air current by 500 degrees C for 3 hours, and the silica after the processing was put in into 1.7l. toluene, and was stirred. The toluene solution of the above-mentioned triethyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate and trihexyl aluminium was added to this silica slurry solution, and it stirred at 90 degrees C for 3 hours. Next, 206ml of toluene solutions of the trihexyl aluminium of 1 mol/l was added, and it stirred at 90 more degrees C for 1 hour. Trihexyl aluminium with a superfluous deed of a decantation was removed for the supernatant 5 times using 90-degree C toluene after that. 0. 20ml of 218 mol/l. ISOPARTME (made in [Exxon chemistry company] the U.S.) solutions of deep purple titanium (N-1, 1-dimethyl ethyl) dimethyl (1-(1, 2, 3, 4, 5, -eta)-2, 3 and 4, 5-tetramethyl-2, 4-cyclopentadiene-1-IRU) SHIRANAMINATO (2-) (N) - (eta4-1, 3-pentadiene). In addition to the above-mentioned mixture, it stirred for 3 hours, and the green support catalyst was acquired. It put into the 1.5l. reactor which carried out the vacuum deairing of the interior and carried out the nitrogen purge with hexane 0.8l. which carried out dehydration deoxidation of a part of acquired support catalyst. Total pressure is 8 kg/cm2 at the mixed gas (gas composition is ethylene 700g, 1-butene 25g, and 0.35l. of hydrogen) of ethylene, 1-butene, and hydrogen, using temperature in a container as 75 degrees C. It carried out. By supplying the mixed gas of the above-mentioned composition, it is total pressure 8 kg/cm2. It maintained, the polymerization was performed for 2 hours, and the ethylene polymer was obtained. The obtained ethylene polymer given in the 1st table is an ethylene polymer which has the restrained amorphous section and has the balance of machine physical properties and a moldability, and is ******.

[0042] (Examples 2-7) Except having changed the amount of 1-butene in mixed gas, and hydrogen, it was operated like the example 1 and the ethylene polymer given in the 1st table was obtained. In addition, the polymerization of the examples 3, 4, and 5 was carried out, without putting in 1-butene. The amorphous section of the obtained ethylene polymer is the ethylene polymer which is restrained and has the balance of machine physical properties and a moldability, and is ******.

(Example 8) The ethylene polymer 50 weight section of an example 4 and the ethylene polymer 50 weight section of an example 6 were mixed using the 200-degree C biaxial extruder. ESCR of this ethylene polymer constituent is 1000 hours, and had ESCR which was excellent compared with the constituent of the example 5 of comparison.

[0043] (Examples 1, 2, and 4 of comparison) <the ethylene polymer by the Ziegler catalyst> -- the polymerization of the example 1 of comparison given in Table 1, the ethylene 1-butene copolymer of 2**, and the ethylene homopolymer of the example 4 of comparison was already carried out using chlorination MAGUNESHUMU 6 well-known hydrate, 2-ethyl hexanol, and the Ziegler catalyst adjusted from chlorination MAGUNESHUMU The examples 1 and 2 of comparison of the obtained ethylene polymer have poor machine physical properties compared with the examples 1 and 2 of this invention. This is because the amorphous section is not fully restrained.

(Example 3 of comparison) In the example 1, solution polymerization was performed having used temperature as 160 degrees C, and the ethylene polymer given in Table 1 was obtained. Although the amorphous section of this ethylene polymer is fully restrained, Mw/Mn of an ethylene polymer is narrow and fabricating-operation nature is poor.

(Example 5 of comparison) The ethylene polymer 50 weight section of the example 4 of comparison and the ethylene polymer 50 weight section of an example 6 were mixed using the 200-degree C biaxial extruder. ESCR of this ethylene polymer constituent is 500 hours, and is ******. This is because the amorphous section of the ethylene polymer of the example 4 of comparison is not fully restrained compared with the ethylene polymer of an example 4.

[0044]

[Table 1]

表 1

	MI	MIR	密度 g/cm3	Mw/Mn	LAM cm^{-1}	T_{2c} μsec	T_{33}／T_{2c}	F50 時間
実施例1	1.0	23	0.9242	3.7	21.8	8.48	6.07	N. B.
2	1.0	27	0.9350	4.5	19.3	8.24	5.67	3500
3＊	1.0	31	0.9573	5.5	11.2	7.65	5.44	50
4＊	100	未測定	0.9720	3.2	11.5	7.69	6.18	未測定
5＊	0.01	40	0.9490	6.8	11.0	7.47	6.07	200
6	0.01	36	0.9297	6.0	17	7.94	5.96	N. B.
7	0.01	35	0.9269	5.5	18.3	8.05	6.01	N. B.
比較例1	1.1	33	0.9245	8.8	18.5	8.38	7.69	3000
2	1.1	32	0.9350	8.1	16	8.19	7.26	1000
3	1.2	15	0.9242	2.1	26	8.58	5.34	N. B.
4＊	103	未測定	0.9725	11	12.2	7.64	7.21	未測定

＊はエチレン単独重合体を表す。N. B. は破壊せずを表す。

[0045]

[Effect of the Invention] It excels in a moldability, the amorphous section is fully restrained, and the ethylene polymer of this invention is excellent in especially the ductile fracture-proof. This ethylene polymer is an ethylene polymer suitable for the pipe with which application to a film, a blow, a pipe, etc. can be performed, especially a ductile fracture poses a problem. Moreover, it has the physical properties which were excellent also in the bimodal constituent which combined the low-molecular ethylene polymer and macromolecule ethylene polymer of this invention.

[Translation done.]